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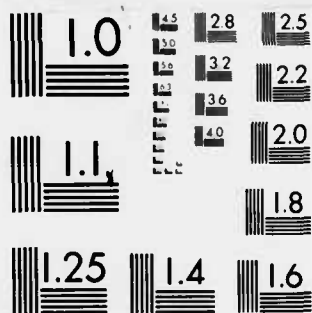
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Electron-Transfer Kinetics of Redox Centers Anchored
to Metal Surfaces: Weak- Versus Strong-Overlap Reaction Pathways

by

S. W. Barr, K. L. Guyer, T. T-T. Li, H. Y. Liu and

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ELECTRON-TRANSFER KINETICS OF REDOX CENTERS ANCHORED TO
METAL SURFACES: WEAK- VERSUS STRONG-OVERLAP REACTION PATHWAYS.

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Abstract

Unimolecular rate constants k_{et} are presented for the one-electron electroreduction of various $Co^{III}(NH_3)_5X$ complexes bound to mercury, platinum, and gold surfaces via either small inorganic or extended organic ligands X. These "surface intramolecular" rate parameters are compared with estimates of k_{et} for outer-sphere pathways obtained from homogeneous rate data in order to ascertain the consequences of reactant-surface binding upon the electron-transfer energetics. Only small or moderate decreases in the elementary reorganization barrier ΔG_{et}^* occur upon surface attachment, suggesting the occurrence of weak-overlap pathways. Aside from the dependence of k_{et} upon the bridging ligand X at a given electrode potential due to differences in thermodynamic driving force, the observed variations in k_{et} appear to be due in part to variations in the electronic transmission coefficient k_{el} . Measurements of electrochemical frequency factors for reactants containing a series of thiophenecarboxylate bridges indicate that the substantial decreases in k_{et} observed upon interruption of ligand conjugation arise predominantly from decreases in k_{el} .

Although electrode processes commonly occur via reaction pathways involving specifically adsorbed intermediates, our understanding of the manner and extent to which the reaction-electrode interactions influence the electron-transfer energetics, i.e., determine the degree of electrocatalysis, is still at a rudimentary level. A difficulty that has hampered the elucidation of such "surface environmental" effects is that the reactions often occur via complex and/or uncertain mechanisms. One approach is to select for detailed study electrode reactions where the reactant, or reaction intermediate, is sufficiently strongly adsorbed to enable unimolecular rate constants (s^{-1}) for the heterogeneous electron-transfer step to be evaluated in addition to the usual rate constants ($cm\ s^{-1}$) for the overall reaction.¹⁻³ We have been interested in examining such systems that also are mechanistically simple, enabling detailed molecular-level interpretation of the rate data to be undertaken.

An especially tractable class of "model reactions" are one-electron transition-metal redox couples



where the solution species Ox and Red are substitutionally inert and bind strongly to the surface via a suitable coordinated ligand.¹⁻³ Such electrode reaction pathways can be labeled "inner sphere" by analogy with homogeneous electron-transfer processes between a pair of metal ions bound via a common ligand. Providing that the electron-transfer step is rate determining, the overall ("apparent") rate constant, k_{app}^{is} (cm s⁻¹), for reaction (1) can be expressed simply as²⁻⁶

$$k_{app}^{is} = K_p^{is} k_{et}^{is} \quad (2)$$

where K_p^{is} is the stability constant for forming the adsorbed ("precursor") state from the bulk reactant, and k_{et}^{is} (s⁻¹) is the rate constant for the elementary electron-transfer step involving the surface-attached intermediate. This "preequilibrium" treatment provides a convenient separation between electrocatalytic influences upon k_{app}^{is} arising from variations in the cross-sectional reactant concentration at the electrode surface, contained in K_p^{is} , and those due to variations in the electron-transfer energetics themselves, embodied in k_{et}^{is} .

Fundamental information on the surface environmental factors influencing k_{app} can therefore be obtained by examining separately the sensitivity of k_{et}^{is} as well as K_p^{is} to variations in the electrode composition and the structure of the bridging ligand.³⁻⁵ We have demonstrated that a number of cobalt(III) and chromium(III) complexes are sufficiently strongly adsorbed at several metal surfaces, especially mercury, silver, platinum, gold, and copper, to enable values of k_{et} to be obtained for the one-electron reduction of the surface-bound redox center.^{2,3} These complexes contain a simple inorganic (Cl⁻, Br⁻, NCS⁻, N₃⁻) or an organic ligand (e.g. pyrazine, 4,4'-bipyridine, thiophenecarboxylates) featuring a halide, nitrogen, or sulfur lone pair as a surface "lead-in" group. These processes are closely analogous to the intramolecular reduction of Co(III) by homogeneous reducing centers such as Ru(II) and Fe(II) that have been extensively investigated in the last few years.⁷ They therefore can be perceived as "surface intramolecular" reactions.

In this conference paper, we shall briefly present some of our recent results, chiefly for reductions of pentaamminecobalt(III), in order to illustrate the virtues of such strategies for unraveling the structural factors influencing the kinetics of electrocatalytic reactions. More complete descriptions of these results along with the experimental details are available elsewhere.^{2,3}

Rate Formulations

Rate constants for surface-bound as well as other "intramolecular" reactions are related directly to the reorganization free energy for

the elementary electron-transfer step ΔG_{et}^* by 6,8

$$k_{et} = \kappa_{el} \Gamma_n \nu_n \exp(\Delta G_{et}^*/RT) \quad (3)$$

The nuclear frequency factor ν_n (sec^{-1}) describes the effective frequency with which the configuration of the various nuclear coordinated appropriate for electron transfer is approached from the precursor state. The electronic transmission coefficient κ_{el} denotes the probability that electron transfer will occur once the transition state is reached. The nuclear tunneling factor Γ_n is a quantum-mechanical correction which accounts for the contribution to the measured rate from molecules which react without entirely surmounting the classical free-energy barrier.^{6,8} Although ν_n is a composite term arising from a weighted mean of manifold frequencies associated with reactant vibration and solvent reorientation modes, it will be close to $1 \times 10^{13} \text{ sec}^{-1}$ for reactions, such as those considered here, where inner-shell reorganization provides an important component of ΔG_{et}^* .⁶ The nuclear tunneling factor Γ_n is usually close to unity (ca. 1-4) at room temperature. However, κ_{el} may well be orders of magnitude below unity if the electronic coupling between the donor and acceptor orbitals is weak (vide infra).

The reorganization energy ΔG_{et}^* at a given electrode potential E can be separated into "intrinsic" and "thermodynamic" contributions:⁴

$$\Delta G_{et}^* = \Delta G_{int}^* + \alpha_{et} [RT(\ln K_p - \ln K_s) + F(E - E^\circ)] \quad (4)$$

Here α_{et} is the transfer coefficient for the elementary step (≈ 0.5), K_s is the equilibrium constant for forming the successor state (i.e. the ground state immediately following electron transfer) from the bulk product, and E° is the standard potential for the redox couple. The "intrinsic barrier" ΔG_{int}^* is the value of ΔG_{et}^* that remains when the free energies of the precursor and successor states are equal.⁴ It is of particular interest since it is the free energy barrier usually calculated from contemporary electron-transfer theories. The first and second sets of terms in parentheses in Eq (4) constitute "surface" and "bulk" components, respectively, of the thermodynamic driving force for the elementary electron-transfer step.

Consequences of Surface Attachment Upon Electron-Transfer Energetics

A central question in the examination of electrocatalytic reactions is to what extent the elementary barrier to electron transfer is modified by binding the reactant to the electrode surface. In view of Eq (3), the rate constant k_{et} for passage over this barrier may well be increased by surface attachment as a result of an increase in κ_{el} as well as from a decrease in ΔG_{et}^* . Such variations in κ_{el} are characteristic of "weak overlap" reactions where the metal

redox center is almost entirely insulated from the electron donor (or acceptor) site provided by the electrode surface. On the other hand, variations in ΔG_{et}^* , more specifically in ΔG_{nt}^* , are characteristic of "strong overlap" reactions. Here $\kappa_{el} \approx 1$ and the interaction with the electron donor (or acceptor) site is sufficient to significantly distort the reactant and product potential-energy surfaces in the intersection region so that the net free energy barrier is "rounded off",⁹ thereby decreasing ΔG_{nt}^* and increasing k_{et} .

At first sight, the question of the influence of surface attachment upon k_{et} may seem hypothetical since values of k_{et} cannot usually be measured directly for unattached reactants. Nevertheless, the preequilibrium rate formalism embodied in Eqs (2) and (3) also applies to outer-sphere pathways;⁶ i.e. those where the reactant in the transition state is separated from the electrode surface by at least one layer of solvent molecules.¹⁰ For such processes the precursor stability constant K_p^{OS} can be estimated from⁶

$$K_p^{OS} = \delta r \exp(-w_p/RT) \quad (5)$$

where w_p is the average work involved in transporting the reactant from the bulk solution to the reaction site (precursor state), and δr is the effective thickness of the reaction zone. The latter equals the effective distances from the plane of closest approach over which electron tunneling can occur with sufficient probability to contribute significantly to the observed rate. Although the typical values of δr are uncertain, it is probably within a factor of two of ca. 1×10^{-8} cm for structurally simple reactants.⁶ The average work term w_p can simply be estimated from $w_p = ZF\phi_r$, where Z is the reactant charge number and ϕ_r is the average potential at the reaction site. An essentially equivalent formalism to this "encounter preequilibrium" model has been employed recently for outer-sphere redox reactions in homogeneous solution.⁸ Besides their practical value, such treatments are fundamentally more correct than the gas-phase collisional model which commonly has been employed for describing outer-sphere reactions.⁶

Admittedly, electrode reactions usually follow rate-dominating inner-, rather than outer-, sphere pathways for reactants featuring surface attachment sites. Consequently, apparent rate constants and hence values of k_{et} for outer-sphere pathways, k_{et}^{OS} , will be unobtainable, at least within the same surface environment for which values of k_{et} for inner-sphere pathways, k_{et}^{IS} , are determined. Nevertheless, the desired estimates of k_{et}^{OS} can be obtained by several routes as follows:

Method I: Suitable chemical modification of the electrode surface, such as the monolayer adsorption of iodide or an under-potential deposited (upd) metal, can eliminate the competing inner-

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sphere route, enabling k_{et}^{OS} to be obtained from the measured value of k_{et}^{OS} , provided that k_p^{OS} can be estimated from double-layer structural data.^{3a,11}

Method II: At least relative values of k_{et}^{OS} at a given electrode potential E for a series of structurally related reactants may be obtained directly from the corresponding second-order rate constants, k_h , for their homogeneous reduction (or oxidation) with a suitable reagent (e.g. $Ru(NH_3)_6^{2+}$) that constrains the reaction to occur by an outer-sphere pathway.^{6,3a} Thus providing k_p^{OS} is approximately the same for each reactant,

$$(k_{et,1}^{OS}/k_{et,2}^{OS})_E = (k_{h,1}/k_{h,2})_R \quad (6)$$

where the subscripts 1 and 2 refer to a pair of reactants, and R refers to a fixed homogeneous coreactant. This relationship follows from the "weak overlap" model of Marcus and others,¹² and has been shown to apply to a number of reactions involving transition-metal complexes.^{11,13,14} Additionally, if one or more of the electrochemical rate constants is known to refer to an outer-sphere pathway, Eq (6) can be utilized to obtain estimates of k_{et}^{OS} for the remaining members of the series.

Method III: For reactants where the surface attachment site is relatively remote from the redox center, such as for extended organic bridges, k_{et}^{OS} may be identified approximately with that obtained for a related reactant containing a similar ligand that lacks the surface-binding group.^{3c}

Methods II and III will be utilized here. Various illustrative kinetic data for the one-electron reduction of fifteen $Co^{III}(NH_3)_5X$ complexes (RoX) are gathered in Tables IA and B. With the exception of OH_2 , NH_3 , F^- and acetate (OAc^-), all the ligands X feature a lone pair on a nitrogen, sulfur, or halide atom which induces sufficiently strong binding at suitable metal surfaces to enable the extent of reactant adsorption, and hence k_{et}^{IS} , to be measured. The values of k_{et}^{IS} given in Table I were obtained either from the corresponding apparent rate constants k_{app}^{IS} combined with K^{IS} [Eq (2)] or directly from the transient currents for reduction of the initially adsorbed species. Details are given elsewhere.^{2,3} The precursor stability constant K^{IS} was determined from $K^{IS} = \Gamma_p/C_b$ (cm), where Γ_p is the surface concentration (mole cm^{-2}) in the precursor state at a given electrode potential, and C_b (mole cm^{-3}) is the corresponding bulk reactant concentration. Mercury-, platinum-, and gold-aqueous interfaces were selected for detailed study of these reactions. The polarizable potential range at platinum and gold extends to sufficiently positive values to enable kinetic data to be obtained even for the most reactive complexes. The mercury-aqueous interface provides an especially suitable surface with which to obtain outer-,

as well as inner-, sphere rate data in view of its reproducibility and well-defined structure. The values of Γ_p were obtained primarily using rapid linear sweep voltammetry and, at mercury, by additionally using chronocoulometry.^{2,3} The rate constants in Table I all refer to a common electrode potential, 0 mV vs. sce. This choice, although somewhat arbitrary, was made so to minimize the extent of data extrapolation that was involved. The relative values of k_{et} are approximately independent of the potential chosen.

Outer-sphere values of $k_{et}^{os,Hg}$, are listed in parentheses in Table I for the four $Co^{III}(NH_3)_5X$ reductions, $X = OH_2, NH_3, F^-,$ and OAc^- , expected to refer to outer-sphere electrochemical pathways at mercury electrodes. These were obtained from the apparent rate constants at mercury in $NaClO_4$ and/or KPF_6 electrolytes by using Eq (3) with $\delta r = 1 \times 10^{-8}$ cm, w_p being estimated from the diffuse-layer potentials, ϕ_r , as described in refs. 15 and 16.

Values of k_{et}^{os} are also given for most other reactions in Table I. These values, labelled $k_{et}^{os,Ru}$, $k_{et}^{os,Cr}$, and $k_{et}^{os,Fe}$, refer to the homogeneous reduction of a given $Co^{III}(NH_3)_5X$ complex by $Ru(NH_3)_6^{2+}$, $Cr(bpy)_3^{2+}$ ($bpy = 2,2'$ -bipyridine), and $Fe(CN)_6^{4-}$, respectively.^{3,6} They were obtained from the corresponding second-order rate constants for reduction of each complex relative to that for $Co(NH_3)_5OH_2^{3+}$ reduction (Method II). The values of k_{et}^{os} were derived by combining these relative values of k_{et}^{os} with the estimate of $k_{et}^{os,Hg}$ for $Co(NH_3)_5OH_2^{3+}$ reduction, ca $2 \times 10^3 \text{ sec}^{-1}$, obtained at the mercury-aqueous interface at 0 mV vs sce. The validity of this procedure is supported by the approximate agreement (within ca. two fold) between the corresponding values of $k_{et}^{os,Hg}$, $k_{et}^{os,Ru}$, and $k_{et}^{os,Cr}$, although somewhat larger differences in these quantities are seen for $Co(NH_3)_5OAc^{2+}$ reduction (Table I).

Close examination of values of k_{et}^{is} and k_{et}^{os} reveals several interesting trends. Broadly speaking, the variations in k_{et} for the surface-attached reactants obtained by altering the bridging group X follow those for the corresponding values of k_{et} for outer-sphere homogeneous environments. This indicates that the reorganization barrier to electron transfer is not greatly altered by surface attachment via these bridging ligands. In other words, the substantially larger rate constants for the overall reaction at mercury, k_{app}^{Hg} , seen for reactions following ligand-bridged pathways (Table I) can be attributed in large part to the increases in K_p , i.e. the greater cross-sectional reactant concentrations at the electrode surface, brought about by reactant-surface bond formation.

Nevertheless, significant differences in k_{et} are seen for a number of reactants in the various reaction environments. Thus for $X^- = NCS^-, Br^-,$ and Cl^- , k_{et} differs by up to 100-fold between the corresponding values obtained for inner-sphere electrochemical, and outer-sphere homogeneous, reaction environments. The values of k_{et}^{os}

are not expected to depend significantly upon the reaction environment. However, the homogeneous reductants $\text{Ru}(\text{NH}_3)_6^{2+}$ and $\text{Cr}(\text{bpy})_3^{2+}$ yield larger values of $k_{\text{et}}^{\text{os}}$, yet the reductant $\text{Fe}(\text{CN})_6^{4-}$ yields smaller values than those of $k_{\text{et}}^{\text{is}}$ obtained for the corresponding inner-sphere electrochemical pathway. Moreover, the values of $k_{\text{et}}^{\text{is}}$ for $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ relative to those for $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$ reduction at gold and platinum are 200 and 2×10^3 , respectively; although comparable ratios of $k_{\text{et}}^{\text{os}}$ are seen for $\text{Ru}(\text{NH}_3)_6^{2+}$ and $\text{Cr}(\text{bpy})_3^{2+}$ (4×10^2 and 75, respectively), the corresponding $k_{\text{et}}^{\text{os}}$ ratio is only ca 6 for reduction by $\text{Fe}(\text{CN})_6^{4-}$. These results suggest that the reactant orientation can have an important influence upon k_{et} . Thus the anionic ligand NCS^- or Cl^- is anticipated to be oriented towards the cationic reductants $\text{Ru}(\text{NH}_3)_6^{2+}$ and $\text{Cr}(\text{bpy})_3^{2+}$, but away from the anionic reductant $\text{Fe}(\text{CN})_6^{4-}$. However, "strong overlap" pathways are very unlikely for outer-sphere reactions. Therefore the much larger values of $k_{\text{et}}^{\text{is}}$ for $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ relative to $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$ reduction at gold and platinum may well be associated with the necessary orientation of anionic ligands towards the electrode, rather than any diminution of the reorganization barrier caused by binding the reactant to the metal surface.^{3a} The origin of such orientation effects may lie in the increased orbital overlap, and hence larger values of κ_{el} , brought about by interposing chloride (or bromide) ligands between the donor and acceptor orbitals located at the metal surface and $\text{Co}(\text{III})$, respectively.

In order to more fully understand the effects of varying the bridging ligand X upon the intramolecular reactivity, it is necessary to estimate the variations in the thermodynamic driving force term $[RT(\ln K_p - \ln K_s) + F(E - E^\circ)]$ in Eq (4). Although to a first approximation the "surface" component $RT(\ln K_p - \ln K_s)$ can be neglected since we expect that $K_p \approx K_s$, at a given electrode potential the "bulk" driving force $F(E - E^\circ)$ may vary greatly due to the dependence of the standard potential E° on the ligand structure. Although values of E° are largely unknown for the present $\text{Co}(\text{III})/(\text{II})$ couples, information on the likely variations in E° with X can be obtained as follows.

The variation in k_{et} relative to that for $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$ reduction, $k_{\text{et}}^{\text{OH}_2}$, caused by variations in the driving force term $F(E - E^\circ)$ can be expressed as

$$k_{\text{et}}^{\text{th}} = k_{\text{et}}^{\text{OH}_2} (K_{\text{II}}/K_{\text{III}})^{1/2} \quad (7)$$

where K_{III} is the equilibrium constant for $\text{Co}^{\text{III}}(\text{NH}_3)_5\text{OH}_2 + \text{X} \rightleftharpoons \text{Co}^{\text{III}}(\text{NH}_3)_5\text{X}$, and K_{II} is the equilibrium constant for formation of the corresponding $\text{Co}(\text{II})$ complex. Although values of K_{II} are unknown, they are expected to be in most cases smaller and markedly less dependent on X than are the values of K_{III} in view of the difference in electronic configuration between $\text{Co}(\text{III})$ and $\text{Co}(\text{II})$ (t_{2g}^6 and $t_{2g}^5 e_g^2$, respectively). Therefore an approximate (and probably limiting) estimate of the expected driving force effects upon k_{et} can

be obtained by inserting the appropriate literature values of K_{III} into Eq (7), along with the experimental value of k_{et}^{OH2} , taking K_{II} as a constant.

The resulting "thermodynamic" estimates of k_{et} , k_{et}^{th} , are also listed in Table IA. (The sources of K_{III} are given in the footnote to Table I. The value of K_{II} was taken as $0.1 M^{-1}$; although somewhat arbitrary, this choice is intuitively reasonable given that Co(II) is expected to have some affinity for anionic ligands relative to H_2O , the value $K_{II} \approx 0.02 M^{-1}$ corresponding to an absence of such affinity). Comparison of the values of k_{et}^{OS} and k_{et}^{IS} with the corresponding estimates k_{et}^{th} shows that the observed variations of k_{et}^{IS} as well as k_{et}^{OS} with the nature of X are in large part accounted for by this "thermodynamic" component, although the values of k_{et} for $Co(NH_3)_5Cl^{2+}$ and $Co(NH_3)_5Br^{2+}$ reduction in electrochemical ligand-bridged and cationic outer-sphere environments are somewhat larger than expected on this basis. We therefore conclude that binding Co(III) to the electrode surface via simple halide or pseudohalide ligands produces only relatively minor changes in the elementary electron-transfer barrier, although some "inner-sphere catalysis" does occur for chloride and bromide ligands at platinum and gold. The latter, nonetheless, may be due to increases in k_{el} caused by more favorable electronic coupling rather than to diminutions in ΔG_{in}^* caused by the occurrence of "strong overlap" reaction pathways.

Turning now to the organic ligand-bridged reactions, comparison of k_{et} values for the seven thiophene-attached reactants in Table IB provide further evidence of the occurrence of electronic coupling effects. The k_{et}^{IS} values at mercury for the reactants featuring uninterrupted conjugation between Co(III) and the sulfur surface binding site are relatively constant ($25-30 sec^{-1}$) and close to k_{et}^{OS} for $Co(NH_3)_5OAc^{2+}$ reduction. However, k_{et}^{IS} for reactants containing one or more saturated carbons between the carboxylate group and the thiophene ring are 10- to 20-fold smaller (Table I). In contrast, k_{et}^{OS} for $Ru(NH_3)_6^{2+}$ reduction of these complexes show only a relatively small dependence on the thiophenecarboxylate structure, the nonconjugated ligands yielding somewhat larger k_{et}^{OS} values than the conjugated systems. This indicates that the smaller k_{et}^{IS} values for the former systems at mercury are characteristic of the ligand-bridged mechanism itself, rather than to variations in the properties of the isolated Co(III) redox center such as the E° values. The most likely explanation is that the electronic coupling between the Co(III) acceptor and surface donor orbitals is sufficiently weak for the nonconjugated ligands to yield smaller values of k_{el} , and hence smaller k_{et}^{IS} values [Eq (3)], than for the conjugated ligands. This is supported by the activation parameter data discussed below. The absence of further decreases in k_{et}^{IS} as the number of saturated carbons is increased from one to three may well be due to the involvement of an alternative reaction pathway where the electron tunnels "directly" between the surface and the Co(III) rather than via the bridging

ligand. Interestingly, these ligand conjugation effects are absent for the reduction of the surface-bound thiophene complexes at gold, the relative values of k_{et}^{is} following instead the $k_{et}^{OS,Ru}$ values (Table I). One explanation is that the mode of adsorption of the bridging ligand at gold differs from that at mercury, the thiophene ring possibly lying flat or the carboxyl oxygen binding to the metal in the former case. This may enable reasonable electronic coupling to be maintained even in the absence of bridging ligand conjugation.

Activation Parameters for Surface-Bound Reactants

In addition to the evaluation of k_{et}^{is} at a single temperature, valuable information on the factors influencing the electron-transfer energetics for surface-bound reactants may be obtained from measurements of electrochemical activation parameters. We have recently discussed their significance for surface-bound reactants.¹⁷ Since neither the standard potentials nor their temperature dependences are known with any accuracy for the present systems, so-called "ideal" activation enthalpies ΔH_i^\ddagger were determined from Arrhenius plots of $\ln k_{et}^{is}$ against $(1/T)$ at a constant cell potential using a nonisothermal cell arrangement. These measurements enable the frequency factor for the elementary electron-transfer step, $A_{et} [= \nu_n \kappa_{el} \Gamma_n]$, Eq (3), to be determined from

$$\ln A_{et} = \ln k_{et}^{is} + \Delta H_i^\ddagger / RT - \Delta S_i^\ddagger / R \quad (8)$$

where ΔS_i^\ddagger is the "ideal" activation entropy. Although ΔS_i^\ddagger is not negligible it can be estimated from $\Delta S_i^\ddagger = 0.5 \Delta S_{et}^\circ$, where ΔS_{et}° is the entropic driving force ("reaction entropy") for the electron-transfer step. For the present Co(III)/(II) couples, on the basis of the available reaction entropy data¹⁸ ΔS_{et}° is expected to lie in the range 20-30 e.u.

Values of ΔH_i^\ddagger and A_{et} for reduction of selected surface-bound reactants at mercury electrodes are summarized in Table II. Since the estimated values of ΔS_{et}° have uncertainties in the range ca 5 - 10 e.u., the resulting frequency factors A_{et} may be up to 3 to 10-fold in error. Nevertheless, the relative values of A_{et} , particularly for structurally similar reactants, are more reliable. The two Cr(III) reactants both yield values of A_{et} that are close to the value, $1 \times 10^{13} \text{ sec}^{-1}$, expected for adiabatic pathways ($\kappa_{el} \approx 1$) for which $A_{et} \approx \nu_n$. The A_{et} values for the two Co(III) reactants, $\text{Co(en)}_2(\text{NCS})_2$ (I)ⁿ and $\text{Co}(\text{NH}_3)_5(2\text{-thiophene acrylate})^{2+}$ (IV) (both $1 \times 10^{12} \text{ sec}^{-1}$), suggest that these reactants are also close to being adiabatic ($\kappa_{el} \approx 0.1$). However, the remaining thiophene complexes (V, VI, VII) which have interrupted conjugation exhibit markedly (10^2 to 10^3 -fold) smaller values of A_{et} as well as k_{et}^{is} . This supports the above suggestion that the smaller reactivity of

these latter complexes arises from the weaker electronic coupling (i.e. smaller values of κ_{el}) brought about by the interposition of saturated carbon atoms between the donor and acceptor sites.

Conclusions

The foregoing analyses indicate that attachment of Co(III) to mercury, platinum, and gold surfaces via either simple inorganic or organic bridging groups yields only small or moderate changes in the elementary reorganization barrier ΔG^* . Thus the corresponding values of k_{et}^{is} and of k_{et}^{os} obtained either in other reaction environments or estimated from the reactivities of structurally similar reactants are typically within ca. 5- to 30-fold of each other. In addition to the influence of the bridging ligand upon k_{et} arising from variations in the thermodynamic driving force, the dependence of k_{et} on the nature of the bridging ligand appears to arise in part from alterations in κ_{el} as a result of changes in the degree of electronic coupling between the surface donor and Co(III) acceptor orbitals. These reactions can therefore be considered to involve weak- rather than strong-overlap electron transfer. The possible exceptions are halide bridges at platinum and gold, where the surface bonds are expected to be relatively covalent, thereby weakening the Co(III)-halide bonds and decreasing the component of ΔG^* and hence ΔG_{in}^* associated with the inner-shell (metal-ligand) reorganization energy. However, the relatively large values of k_{et}^{is} observed for these reactions can be attributed in part to increases in κ_{el} arising from the enhanced electronic coupling provided by the interposition of the monoatomic ligand between the donor and acceptor orbitals.

The experimental frequency factors for the surface intramolecular reactions at mercury, $A_{et} \approx 10^{10}$ to 10^{13} sec⁻¹, suggest that κ_{el} lies in the region ca 10^{-3} - 1 (i.e. nonadiabatic pathways occur), although κ_{el} probably approaches unity (i.e. adiabaticity is achieved) with small inorganic bridging ligands. These conclusions are similar to those from recent experimental and theoretical work for related homogeneous electron-transfer processes. Thus values of κ_{el} substantially below unity are predicted for some homogeneous outer-sphere reactions even at small internuclear separations (5-6 Å).¹⁹ Nonadiabatic pathways for homogeneous intramolecular Co(III) - Ru(II) reactions bridged by bipyridine ligands featuring interrupted conjugation are also evidenced by the values of A_{et} obtained for these processes,⁷ especially after correction for the entropic driving force.²⁰

It is interesting to compare this situation with the catalyses induced by the ligand-bridged reduction of $Co^{III}(NH_3)_5X$ complexes by homogeneous reagents such as Cr^{2+} , Eu^{2+} , V^{2+} , and Fe^{2+} . The analysis of the reaction energetics is considerably more tenuous than for the electrochemical reactions since little information is available on the

precursor complex stabilities K_{15}^{is} . Moreover, the comparison of rate constants for corresponding outer- and inner-sphere pathways is less straightforward for homogeneous reactions since cognizance must be taken of the contribution to the reorganization energy from the coreactant. This component will probably be different for the outer- and inner-sphere routes since the coreactant's coordination sphere will necessarily be altered in forming the precursor complex.

Nevertheless, some useful deductions can be made from the available rate data. The most remarkable ligand-bridged rate accelerations occur for reductions by Cr^{2+} ; for example, $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ is reduced by Cr^{2+} nearly 10^{10} fold more rapidly than is $\text{Co}(\text{NH}_3)_6^{3+}$.²¹ The corresponding rate ratios for reduction by V^{2+} and Eu^{2+} are about 10^4 , similar to that for $\text{Ru}(\text{NH}_3)_6^{2+}$ (Table I).²¹ The $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ - Cr^{2+} reaction clearly follows an inner-sphere pathway, whereas the latter two processes may follow outer-sphere mechanisms. Although the binding constant of Cr^{2+} to $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ is unknown, it would need to be ca 10^6 -fold higher than for the other reagents to account for the additional rate acceleration, which is highly implausible. Therefore this, and also other ligand-bridged $\text{Co}(\text{III})(\text{NH}_3)_5\text{X}$ - Cr^{2+} reactions seem certain to occur via "strong overlap" pathways, i.e. where the elementary electron-transfer barrier $\Delta G_{\text{et}}^{\ddagger}$ is lowered substantially by electronic interactions between the redox centers.⁴

There have been several recent discussions of the factors influencing such inner-sphere catalyses.^{22,23} It suffices to note here that such rate enhancements appear to be dependent upon the symmetry of the donor and acceptor orbitals, the most dramatic rate accelerations occurring for systems where both orbitals have e_g symmetry.²² For such systems, it has recently been suggested that the precursor formation and electron-transfer steps are merged such that the bridge forms a "three-center" bond with the two metal cations.²³ The absence of such dramatic catalyses for the electrochemical reduction reactions is probably related to the relatively weak electronic coupling expected between the surface and $\text{Co}(\text{III})$ e_g acceptor orbitals, although the donor orbitals at gold and especially platinum surfaces are expected to have some d orbital character. Nevertheless, strong-overlap electron transfer may well occur for electrochemical processes involving adsorbed redox centers, such as oxygen, which bind directly to metal surfaces rather than via a bridging group.

The evaluation of electrochemical rate constants and activation parameters for surface-bound reactants, especially for a series of structurally related systems, clearly provides detailed information on the electron-transfer energetics that are unavailable from measurements of electrochemical reactivities for bulk-phase reactants. We anticipate that a wealth of hitherto unavailable information on the factors influencing the degree of adiabaticity of heterogeneous electron-transfer reactions can be extracted from systematic studies of the dependence of A_{et} as well as k_{et} on the structure of the metal redox center, the metal surface, and the mediating group.

Acknowledgements

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



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TABLE IA. Unimolecular Rate Constants (s^{-1}) for Reduction of $Co(NH_3)_5X$ Complexes Containing Inorganic Bridging Ligands X at 0 mV vs sce in $0.1M NaClO_4$

Reactant ^a	k_{app} cm sec ⁻¹	Electrochemical ^b Hg ket is, Au ket	$k_{is, Pt}$ ket	$k_{os, Ru}$ ket	Homogeneous ^c $k_{os, Cr}$ ket	$k_{os, Fe}$ ket	k_{th} ket
$RoOH_2^{3+}$	5×10^{-4}	(2×10^3)		$[2 \times 10^3]$	$[2 \times 10^3]$	$[2 \times 10^3]$	$[2 \times 10^3]$
$RoNH_3^{3+}$	1.5×10^{-6}	(10)		6			~10
RoF^{2+}	2×10^{-6}	(1×10^2)		200			~100
$RoAc^{2+}$	2×10^{-6}	(80)		10	50	4	~50
$RoNCS^{2+}$	3×10^{-3}	25	1.5	5×10^2	4×10^2	50	~30
RoN_3^{2+}	3×10^{-4}	20 (~20)		1×10^3	1.5×10^3	25	~30
$RoCl^{2+}$	>0.1	6×10^3	3×10^3	2×10^5	3×10^4	3×10^2	~ 5×10^2
$RoBr^{2+}$	>0.1	8×10^3	1.5×10^3	1×10^6	2×10^5		~ 1×10^3

For Table IB and footnotes, see following page.

TABLE IB. Unimolecular Rate Constants (s^{-1}) for Reduction of $Co(NH_3)_5X$ Complexes Containing Thiophenecarboxylate Bridging Ligands X at 0 mV vs sce in 0.1 M $NaClO_4$

Reactant	Electrochemical		Homogeneous	
	k_{app}^{Hg} $cm\ sec^{-1}$	k_{et}^{Hg}	$k_{et}^{is,Au}$	$k_{et}^{os,Ru}$
$RoOH_2^{3+}$	5×10^{-4}	(2×10^3)		$[2 \times 10^3]$
$RoAc^{2+}$	2×10^{-6}	(80)		10
 $COORo^{2+}$	2×10^{-3}	25	3	7
 CH_2COORo^{2+}	4×10^{-4}	2.5	5	20
 $(CH_2)_2COORo^{2+}$	6×10^{-4}	2.5	6	20
 $(CH_2)_3COORo^{2+}$	3×10^{-4}	2	3	6
 $CH=CHCOORo^{2+}$	3×10^{-3}	45	6	25
 $COORo^{2+}$	5×10^{-4}	30	7	7
 CH_2COORo^{2+}	5×10^{-4}	1.5	10	10

Footnotes to Tables IA and B.

^a $Ro = Co^{III}(NH_3)_5$, OAc = acetate.

^bApparent (measured) rate constant for overall reaction at mercury-aqueous interface measured using normal pulse or d.c. polarography.

^cUnimolecular rate constant at mercury-aqueous interface. Values without parentheses, k_{et}^{is} , refer to inner-sphere (ligand-bridged) pathway, measured either directly or indirectly from k_{app}^{is} using Eq (2). Values within parentheses, k_{et}^{os} , refer to outer-sphere pathway at mercury, determined from $k_{et}^{os} = k_{app}^{os} / k_{app}^{is}$, with k_{et}^{os} determined from Eq (5) (see text).

^dValue of k_{et}^{is} determined at gold-aqueous interface.

^eValue of k_{et}^{is} determined at platinum-aqueous interface.

^fValue of k_{et} for outer-sphere pathway, k_{et}^{os} , obtained from the value of k_{et} ($2 \times 10^3\ sec^{-1}$) obtained for $Co(NH_3)_5OH_2^{3+}$ reduction at mercury electrodes combined with relative rate constants for homogeneous reduction of $Co(NH_3)_5X$ and $Co(NH_3)_5OH_2^{3+}$ by $Ru(NH_3)_6^{2+}$ [Eq (6)].

[continued over]

^gAs for footnote f, but using $\text{Cr}(2,2\text{'-bipyridine})_3^{2+}$ as outer-sphere reductant.





^hAs for footnote g, but using $\text{Fe}(\text{CN})_6^{4-}$ as outer-sphere reductant.

ⁱValue of k_{et} determined from $k_{\text{et}}^{\text{OH}_2}$ for $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$ ($2 \times 10^3 \text{ sec}^{-1}$) by correcting for changes in thermodynamic driving force ($E-E^\circ$) using Eq (7), with K_{II} taken as 0.1 (see text).

Data Sources: All electrochemical rate data from refs. 3a-c. Homogeneous rate data for $\text{Ru}(\text{NH}_3)_6^{3+}$ reductions: $X = \text{OH}_2, \text{NH}_3, \text{Cl}^-, \text{Br}^-$, J.F. Endicott, H. Taube, J. Am. Chem. Soc. 86, 1686 (1964); $X = \text{F}^-$, R.C. Patel, J.F. Endicott, J. Am. Chem. Soc. 90, 6364 (1968); $X = \text{NCS}^-$, N. Adegite, M. Dosumu, J.F. Ojo, J. Chem. Soc. Dalton, 630 (1977); $X = \text{OAc}^-$, thiophene carboxylates, ref. 3c. Rate data for $\text{Cr}(2,2\text{'-bipyridine})_3^{2+}$ reductions: J.P. Candlin, J. Halpern, D.L. Trimm, J. Am. Chem. Soc. 86, 1019 (1964); Rate data for $\text{Fe}(\text{CN})_6^{4-}$ reductions: D. Gaswick, A. Haim, J. Am. Chem. Soc. 93, 7347 (1971); A Miralles, Ph.D. thesis, State University of New York at Stonybrook, 1974; A. Haim, personal communication.

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TABLE II. Electrochemical Activation Parameters for Reduction of Representative Surface-Bound Co(III) and Cr(III) Reactants at Mercury Electrodes in 0.1 M NaClO₄.

Reactant	E mV vs sce	k_{et}^{is} ^a sec ⁻¹	ΔH_i^* ^b kcal. mol ⁻¹	ΔS_i^* ^c cal.deg ⁻¹ mol ⁻¹	A_{et} ^d sec ⁻¹
I) c-Co(en) ₂ (NCS) ₂ ⁺	-100	0.15	20.5	~10	~1x10 ¹²
II) c-Cr(OH ₂) ₄ (NCS) ₂ ⁺	-600	70	20	~13	~3x10 ¹³
III) f-Cr(OH ₂) ₃ (NCS) ₃	-600	70	16	~ 0	~3x10 ¹³
IV)  -CH=CHCOORo ²⁺	-200	4x10 ³	15.6	~13	~1x10 ¹²
V)  -CH ₂ COORo ²⁺	-200	260	14.1	~13	~1x10 ¹⁰
VI)  -(CH ₂) ₂ COORo ²⁺	-200	290	14.8	~13	~3x10 ¹⁰
VII)  -(CH ₂) ₃ COORo ²⁺	-200	230	13.2	~13	~1x10 ⁹

^aUnimolecular rate constant for reduction of surface-bound Co(III) or Cr(III) complex at stated electrode potential E.

^b"Ideal" activation enthalpy at stated value of E, determined from $\Delta H_i^* = R[\partial \ln k_{et} / \partial (1/T)]_E$ using a nonisothermal cell arrangement.¹⁷

^cEstimated "ideal" activation entropy ΔS_i^* (see text).

^dFrequency factor for elementary electron-transfer reaction, determined from listed values of k_{et}^{is} , ΔH_i^* , and ΔS_i^* .

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$X^- = \text{NCS}^-$, Br^- , and Cl^- , k_{et} differs by up to 100-fold between the corresponding values obtained for inner-sphere electrochemical, and outer-sphere homogeneous, reaction environments. The values of $k_{\text{et}}^{\text{OS}}$

in electronic configuration between Co(III) and Co(II) (t_{2g}^6 and $t_{2g}^5 e_g^2$, respectively). Therefore an approximate (and probably limiting) estimate of the expected driving force effects upon k_{et} can

smaller k_{et}^{15} values [Eq (3)], than for the conjugated ligands. This is supported by the activation parameter data discussed below. The absence of further decreases in k_{et}^{15} as the number of saturated carbons is increased from one to three may well be due to the involvement of an alternative reaction pathway where the electron tunnels "directly" between the surface and the Co(III) rather than via the bridging

being adiabatic ($k_{et} \approx 0.1$). However, the remaining
complexes (V, VI, VII) which have interrupted conjugation exhibit
markedly (10^2 to 10^3 -fold) smaller values of A_{et} as well as k_{et} .
This supports the above suggestion that the smaller reactivity of